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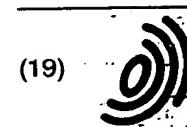
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(54) Layered, hexagonal lithium manganese oxide as a positive electrode active material for lithium battery, method for producing the same, and lithium battery containing the same

(57) An inexpensive positive electrode active material for lithium batteries which comprises lithium manganese having a hexagonal layered structure with space group of R3m and exhibits continuous discharge volt-

age characteristics between 4.5 V and 2 V for metallic lithium.

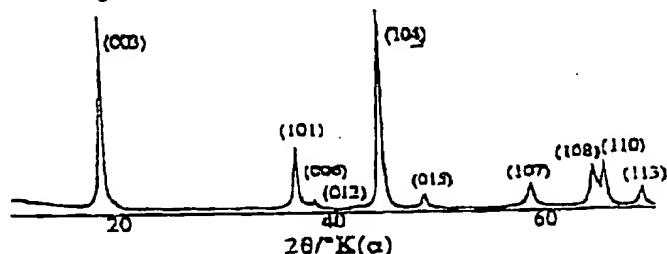


Fig. 1A

Description

1. The present invention relates to a positive electrode having a LiMnO₂ active material, a method for producing the same, and a battery containing the same in the positive electrode thereof.

1. Field of the Invention

The present invention relates to a positive electrode having a LiMnO₂ active material for a lithium battery, a method for producing the same, and a battery containing the same in the positive electrode thereof.

2. Description of the Related Art

With the recent development of portable electronic equipment, batteries of higher performance have been demanded. Lithium ion batteries using a carbon material in the negative electrode and lithium cobaltate (LiCoO₂), which is a composite oxide having a layered structure, in the positive electrode have been put to practical in a nonaqueous battery having a high working voltage and a high energy density. Lithium nickelate (Li-containing nickel oxide; LiNiO₂) is also a compound having the same layered crystal structure as the lithium cobaltate in which lithium ions are intercalated between layers of NiO₆ octahedral sharing edges.

Lithium nickelate is generally prepared by mixing a nickel source selected from Ni(NO₃)₂, Ni(OH)₂, NiCO₃, and NiO, NiOOH, etc. and a lithium source selected from LiOH, LiNO₃, Li₂CO₃, Li₂O₂, etc., and subjecting the mixture to a heat treatment at about 600 to 900°C in an oxygen stream.

Since cobalt or nickel used in these active materials is expensive for scarcity, less expensive active materials for a positive electrode has been sought. For example, Li-containing manganese composite oxide (LiMn₂O₄) having a spinel structure has been proposed; but its theoretical capacity of 148 mAh/g is low, and the reduction in capacity increases with charge and discharge cycles.

LiMnO₂ has been proposed as a promising active material for batteries with higher performance. Among various phases exhibited by LiMnO₂, two phases, whose crystal structure have been well characterized, are a high temperature orthorhombic phase (Pmnmm) and a low temperature tetragonal phase (I41/amd). Both structures involve cubic close packing but they differ in the arrangement of the ordering of the lithium and manganese cations. The tetragonal form Li₂Mn₂O₄ is prepared by electrochemically or chemically intercalating lithium into the spinel LiMn₂O₄[Mat. Res. Bull. 18(1983)461 & 18(1983)1375; J. Electrochem. Soc. 138(1991)2864 & 139(1992)937]. The orthorhombic phase has been prepared mainly by the solid state reaction at high temperature using different precursors [J. Phys. Chem. Solid. 3(1957)20 & 318; J. Phys. Radium 20(1959)155; J. Inorg. Alig. Chem. 417(1975)1; Mater. Res. Bull. 28(1993)1249]. However, orthorhombic LiMnO₂ was reported to be prepared at low temperature using the solid state reaction by heating a mixture of γ -MnOOH and LiOH at 300 to 450°C [Chem. Express,

7(1992)198]. An other process for preparing the orthorhombic LiMnO₂ at a temperature less than 100°C by ion exchange was reported [J. Electrochem. Soc. 140(1993)3396; Unexamined Japanese Patent Publication (kokai) No. 6-349494]. In this case, the exchange was carried out by refluxing γ -MnO₂ under boiling condition in LiOH solution. So far, LiMnO₂ isostructural with layered LiNiO₂ or LiCoO₂ has not yet been synthesized.

Referring to LiMnO₂ having a layer structure, J. Solid State Chem., 104(1993)464 and U.S. Patent 5,153,081 report that LiMnO₂ having a monoclinic layer structure can be obtained by acid leaching of Li₂O out of Li₂MnO₃. In the first step, Li₂MnO₃ was prepared by reacting electrolytic manganese dioxide (EMD) with a stoichiometric quantity of Li₂O₃. The obtained material was then delithiated using H₂SO₄ at room temperature for 64 hours.

The thus obtained substance exhibits a discharge voltage of 3 V vs. Li/Li⁺. Although the reaction product exhibits a new X-ray diffraction peak at 2θ=19.5°, most of the other peaks correspond to the starting material which is Li₂MnO₃ (U.S. Patent 5,153,081). Ignoring the fact that most of the peaks are assigned to the starting Li₂MnO₃, the inventors of U.S. Patent 5,153,081 identify the product to be a substance having a layer structure based on the peak at 2θ=19.5°, but the identification seems to be decisively unreasonable. In this case, the product should rather be regarded as a lithium manganese oxide having a spinel structure as a basic skeleton, such as Li₂Mn₄O₉ or Li₄Mn₅O₁₂.

Further, J. Solid State Chem., 104(1993)464 reports a substance having a layer structure whose X-ray diffraction pattern is different from those of LiNiO₂ or LiCoO₂. While not entering into details about structural refinement of the substance, the report based their layered structure on the assumption that removal of Li₂O from Li₂MnO₃ causes a shearing of the closed-packed oxygen planes to yield an oxygen array in the obtained material comprised of alternate layers of trigonal prisms where lithium is located and sheets of edge-shared octahedra where manganese is located. In this case, the manganese ions remain in alternate layers and do not migrate to the lithium layers during the leaching process, and the lithium layer is arranged in a zig-zag fashion with lithium ions in a trigonal prismatic coordination.

Unexamined Japanese Patent Publication (kokai) No. 7-223819 reports that LiMnO₂ having a layer structure with a lattice constant of a=3.321 Å and c=4.730 Å is obtained by electrolysis method. This material is not isostructural with LiNiO₂. Thus, no LiMnO₂ having a layer structure similar to that of LiNiO₂ or LiCoO₂, has been synthesized yet.

As stated above, although 4.0 V type LiMn₂O₄ having a spinel structure has been proposed as an inexpensive Li-containing manganese composite oxide, the theoretical capacity is inferior to oxide compounds having a hexagonal layer structure, such as LiNiO₂ (theo-

retical capacity: 275 mAh/g) and LiCoO₂ (theoretical capacity: 274 mAh/g). In addition, the charge and discharge cycle characteristics are better in layered oxide materials. Therefore, development of an inexpensive active material having a layer structure similar to that of LiNiO₂ or LiCoO₂ and establishment of synthesis thereof have been keenly demanded, but a useful method of synthesis has not yet been established.

SUMMARY OF THE INVENTION

It is an object of the present invention to prepare lithium manganate with a structure different from the spinel structure of known LiMn₂O₄ but is analogous to the hexagonal layer structure of lithium cobaltate or lithium nickelate, having a space group of R3m, and is therefore expected to exhibit increased activity as a positive electrode active material for lithium batteries.

The present invention provides a positive electrode active material for lithium batteries which comprises lithium manganate having a hexagonal layer structure with the space group of R3m and exhibits continuous discharge voltage characteristics between 4.5 V and 2 V vs. Li/Li⁺. The active material according to the present invention has a theoretical capacity of 286 mAh/g.

The present invention also provides a method for producing such a positive electrode active material and a battery containing the positive electrode active material.

The positive electrode active material according to the present invention undergoes homogeneous reaction to exhibit continuous discharge voltage characteristics between 4.5 V and 2.0 V vs. Li/Li⁺. The discharge characteristics are stable upon cycling, providing a long battery life. The active material of the invention is inexpensive and economical.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A shows an X-ray diffraction patterns of LiMnO₂ having a layer structure according to the present invention; Fig. 1B shows an X-ray diffraction pattern of LiNiO₂ having a layer structure; Fig. 1C shows an X-ray diffraction patterns of LiMnO₂ with orthorhombic structure obtained by a conventional solid phase reaction;

Fig. 2 shows an illustration of the layer structure of LiMnO₂ according to the present invention; and

Fig. 3 shows typical discharge characteristics of LiMnO₂ according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The lithium manganate according to the invention is not the known LiMnO₂ obtained by the reaction between γ -MnOOH and LiOH in a solid phase calcination process but LiMnO₂ which is obtained by a hydrothermal reaction of γ -MnO₂ in an LiOH solution and has

a layer structure similar to the structure of LiNiO₂ or LiCoO₂. The lithium manganate of the present invention can be applied as a positive electrode active material in an nonaqueous solution to provide inexpensive and high-performance batteries.

The active material according to the present invention has a layer structure similar to the structure of LiNiO₂ or LiCoO₂, i.e., a structure similar to α -NaFeO₂.

The layered structure of the active material can be described from a packing MnO₂ slabs built up of edge-sharing MnO₆ octahedra in between which lithium ions are located in the octahedral oxygen environment. This structure comprises a layer of manganese ions in octahedral environment, surrounded by oxygen ions arranged in a cubic close packed arrangement resulting in the formation of sheets of edge-shared octahedra. It also comprises a lithium layer where lithium is having an octahedral environment and is sandwiched between two layers of octahedral MnO₆.

The active material according to the present invention was found to have a layer structure having a lattice constant of $a=2.86$ Å and $c=14.23$ Å similarly to LiNiO₂ or LiCoO₂. The lattice constant is not a fixed one. That is, the unit lattice constant is subject to variation from 2.76 to 2.96 Å as for a , and from 14.18 to 14.33 Å as for c according to the conditions of preparation or by addition of dopant such as nickel, cobalt, zinc, etc. The active material exhibits continuous discharge characteristics between 4.5 V and 2 V vs. Li/Li⁺.

The active material of the invention is preferably produced by dissolving or suspending a starting manganese salt in lithium solution and causing the solution to react in an autoclave under high pressure and low pH solution. Suitable raw manganese materials are inorganic salts such as MnO₂, Mn₂O₃, MnOOH, and MnCO₃, and organic salts such as manganese acetate, manganese butyrate, manganese oxalate, and manganese citrate. Suitable raw lithium materials are LiOH, LiNO₃, Li₂CO₃, Li₂O₂, lithium acetate, lithium butyrate, lithium oxalate, and lithium citrate. Solvents to be used in the reaction are purified water, and organic solvents such as ethyl alcohol, methyl alcohol, acetone, and acetonitrile. The reaction is preferably carried out at a high temperature of from 100 to 300°C.

LiMnO₂ having a layer structure can be synthesized by a hydrothermal process. The high-pressure and low-temperature hydrothermal process, according to the present invention, is also applicable to synthesis of other substances having a layer structure represented by general formula AMeO₂ (A: Li, Na, K, Me: Mn, Ni, Co, Fe, Cr or V).

EXAMPLES

The present invention will be described in greater detail with reference to examples, but it should be understood that the present invention is not constructed as being limited thereto.

668 mg of LiOH was dissolved in 120 ml of water at

50°C, and thereafter, 50 mg of γ -MnO₂ was immersed therein for 30 minutes. The pH of the solution was adjusted to 1 to 2 and the mixture was heated in an polytetrafluoroethylene-covered stainless steel autoclave at 170°C and 300 atm for 5 days to obtain lithium manganate according to the present invention.

10 The X-ray diffraction pattern (CuK α) of the resulting active material is shown in Fig. 1A. For comparison, the diffraction pattern of LiNiO₂ having a layer structure is shown in Fig. 1B, and that of orthorhombic LiMnO₂ obtained by a conventional solid phase reaction (calcination of a mixture of γ -MnO₂ and LiOH at 700°C) is shown in Fig. 1C.

15 It can be seen that the diffraction pattern of the active material of the present invention is not similar to that of known orthorhombic LiMnO₂ but to that of LiNiO₂ having a layer structure. It was found that the indices of a plane of the diffraction peaks can be assigned to the layer structure of hexagonal system having a space group of R3m. The structural description of the active material of the invention is shown in Fig. 2.

20 The active material of the present invention has a packing structure of two MnO₂ layers composed of octahedral of MnO₆ sharing edges, in which a lithium ion is surrounded by oxygen ions having an octahedral coordination. In this structure, manganese ions are arranged in layers and surrounded by an octahedron of oxygen ions which are arranged in cubic closest packing to form an octahedral layer sharing edges. The lithium ion of the lithium layer is sandwiched in between two layers of octahedral of MnO₆.

25 It was found that the structure of the active material of the present invention is similar to the layer structure of LiNiO₂ or LiCoO₂, typically having a unit lattice constant of $a=2.86$ Å and $c=14.23$ Å. The unit volume was 101.23 Å³, approximately the same as 101.3 Å³ of LiNiO₂. This means that the LiMnO₂ having a layer structure and LiNiO₂ are apt to form a solid solution. In fact, addition of nickel to LiMnO₂ results in stabilization of crystal properties, and the resulting solid solution was less susceptible to deterioration by charge and discharge cycles.

30 On the other hand, because of structural difference between orthorhombic LiMnO₂ and LiNiO₂, orthorhombic LiMnO₂ forms a solid solution LiMn_xNi_{1-x}O₂ ($0 \leq x \leq 0.5$), but the solid solution has poor charge and discharge characteristics as reported in Solid State Ionics, 57(1992)311. It was confirmed that addition of cobalt to the active material of the invention produces the same effect. It is understood that the LiMnO₂ having a layer structure according to the invention is different from LiMnO₂ of orthorhombic structure the diffraction pattern of which is shown in Fig. 1C.

35 The active material obtained in this Example had a layer structure of perfect hexagonal system in which no substitution between manganese ions and lithium ions was observed. While structures in which lithium and manganese are substituted with each other were obtained in some cases depending on the temperature

40 and pressure conditions of the hydrothermal reaction, the active material principally had a layer structure.

45 A battery was prepared using thus obtained active material as a positive electrode active material and metallic lithium as a negative electrode. When the battery was charged to 4.2 V at a current of 0.2 C and then discharged to 2 V at the same current, satisfactory electrochemical activity was exhibited. The typical discharge characteristics are shown in Fig. 3. It is seen that stable discharge characteristics can be secured through the charge and discharge cycles. It is also seen that continuous discharge characteristics are exhibited between 4.5 V and 2 V vs. Li/Li⁺, which has not been reported to date. The LiMnO₂ having a layer structure has now been proved to be an unreported inexpensive active material. The LiMnO₂ has a theoretical capacity density of 286 mAh/g. Further optimization of electrode designing will produce higher performance.

50 While the present invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

25 Claims

1. A positive electrode active material for lithium batteries comprising lithium manganate having a hexagonal structure and a space group of R3m, and exhibiting continuous discharge voltage characteristics between 4.5 V and 2 V vs. Li/Li⁺.
2. A positive electrode active material according to claim 1, wherein said lithium manganate has a unit lattice constant of $a=2.76$ to 2.96 Å and $c=14.13$ to 14.33 Å.
3. A positive electrode active material according to claim 1, further comprising at least one of nickel, cobalt, iron, chromium, zinc and vanadium.
4. A battery comprising a positive electrode active material for lithium batteries comprising lithium manganate having a hexagonal structure and a space group of R3m, and exhibiting continuous discharge voltage characteristics between 4.5 V and 2 V vs. Li/Li⁺; and a negative electrode.
5. A battery according to claim 4, wherein said negative electrode comprises metallic lithium, carbon and metal alloys.
6. A battery according to claim 4, wherein said lithium manganate has a unit lattice constant of $a=2.76$ to 2.96 Å and $c=14.13$ to 14.33 Å.
7. A battery according to claim 4, wherein said positive electrode active material further comprises at least one of nickel, cobalt, zinc, iron, chromium and

vanadium.

8. A method for producing a positive electrode active material for lithium batteries wherein a raw manganese material and a raw lithium material are reacted by a hydrothermal process to produce a lithium manganate.

9. A method according to claim 8, wherein said raw manganese material is selected from a group consisting of MnO_2 , Mn_2O_3 , $MnOOH$, $MnCO_3$, manganese acetate, manganese butyrate, manganese oxalate, and manganese citrate, and said raw lithium materials is selected from a group consisting of $LiOH$, $LiNO_3$, Li_2CO_3 , Li_2O , lithium acetate, lithium butyrate, lithium oxalate, and lithium citrate.

10. A method according to claim 8, wherein said hydrothermal process is carried out in a solvent selected from purified water, ethyl alcohol, methyl alcohol, acetone, and acetonitrile.

11. A method according to claim 8, wherein said hydrothermal process is carried out at a temperature of 100°C or higher.

12. A method according to claim 11, wherein said hydrothermal process is carried out at a temperature of 200°C or less.

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Fig. 1C

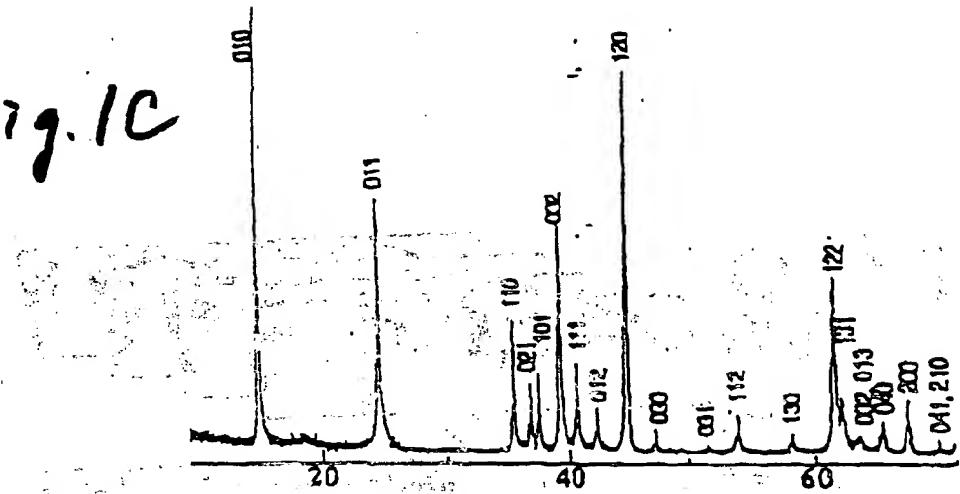


Fig. 1B

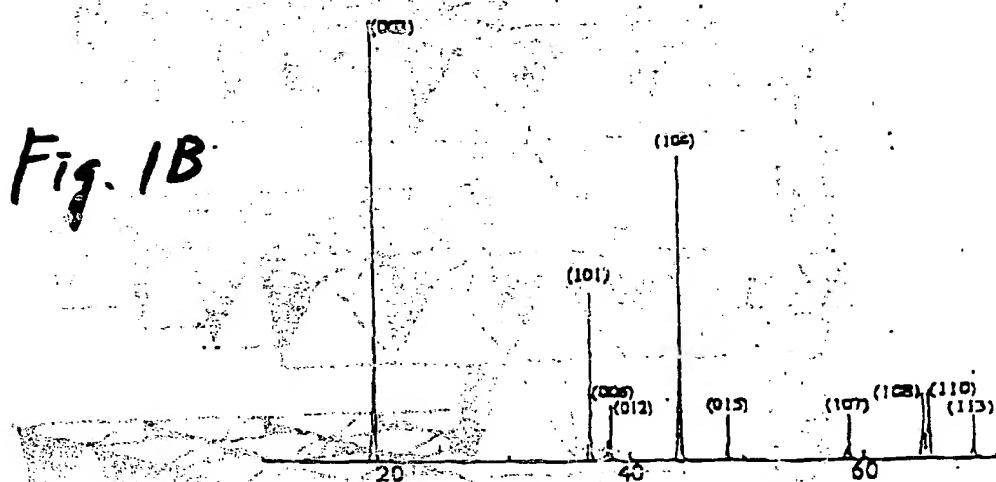


Fig. 1A

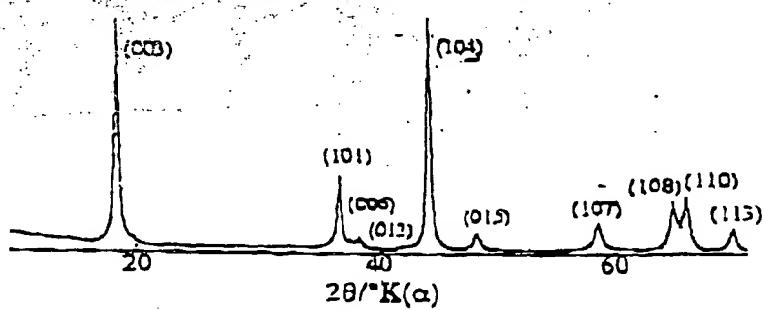


Fig. 2

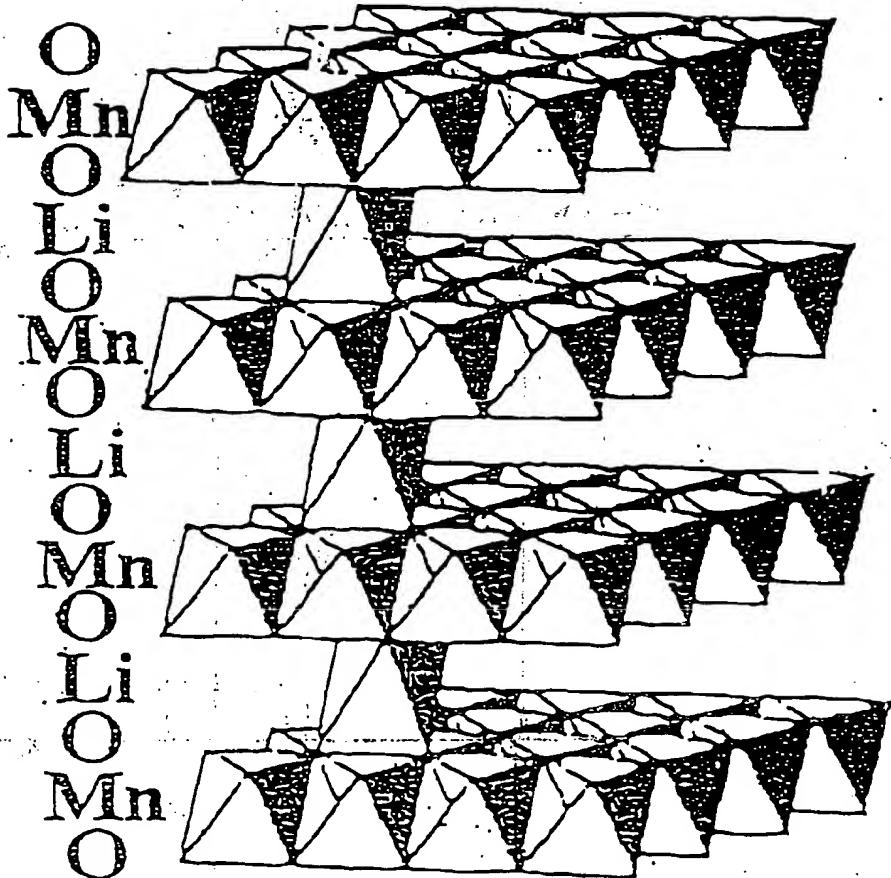
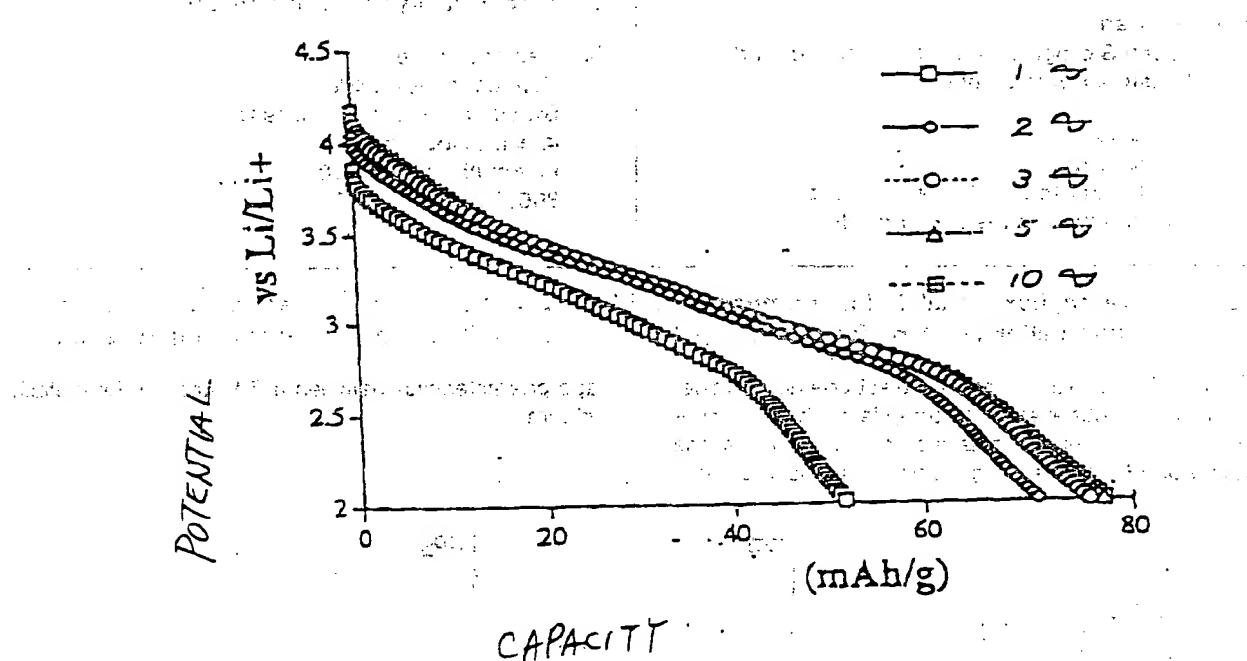
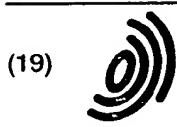


Fig.3





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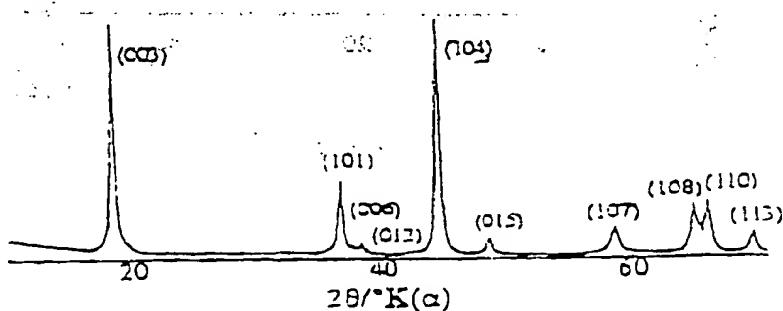
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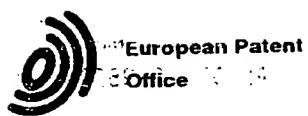
(57) An inexpensive positive electrode active material for lithium batteries which comprises lithium manganese having a hexagonal layered structure with space group of R3m and exhibits continuous discharge volt-

age characteristics between 4.5 V and 2 V for metallic lithium.

Fig. 1A



EP 0 813 256 A3



EUROPEAN SEARCH REPORT

Application Number

EP 97 10 9591

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
P,X	CAPITAINE F ET AL: "A new variety of LiMnO ₂ with a layered structure" SOLID STATE IONICS, vol. 89, no. 3-4, 2 August 1996, page 197-202 XP004069977 * the whole document *	1-7	H01M4/50 H01M10/40 C01G45/12 H01M4/48						
P,X	STROBEL P ET AL: "Synthesis and chimie douce reactions in lithium phyllo manganate" MATERIALS RESEARCH BULLETIN, vol. 31, no. 11, November 1996, page 1417-1426 XP004053631 * Pages 1418, 1419: "Experimental" * * Page 1423 * * table 1 *	1,4							
D,X	US 5 153 081 A (THACKERAY MICHAEL M ET AL) 6 October 1992 * column 1, line 17 - column 2, line 44 * * column 7, line 7 *	1,3-5,7							
Y	PATENT ABSTRACTS OF JAPAN vol. 096, no. 005, 31 May 1996 & JP 08 007883 A (SONY CORP), 12 January 1996, * abstract *	1,4	H01M C01G						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>MUNICH</td> <td>22 July 1998</td> <td>Engl, H</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	MUNICH	22 July 1998	Engl, H
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, Y	<p>CHEMICAL ABSTRACTS, vol. 125, no: 14, 30 September 1996 Columbus, Ohio, US; abstract no: 183936, CAURANT, DANIEL ET AL: "Preparation by a 'chimie douce' route and characterization of LiNizMn1-zO2 (0.5<=z<= 1) cathode materials" XP002072298 * abstract * & J. MATER. CHEM. (1996), 6(7), 1149-1155 CODEN: JMACEP; ISSN: 0959-9428,</p> <p>---</p> <p>CHEMICAL ABSTRACTS, vol. 106, no: 26, 29 June 1987 Columbus, Ohio, US; abstract no. 226231, HEWSTON, T. A. ET AL: "A survey of first-row ternary oxides: lithium metal oxide (LiMO₂) (M = scandium-copper)" XP002072299 * abstract * & J. PHYS. CHEM. SOLIDS (1987), 48(2), 97-108 CODEN: JPCSAW; ISSN: 0022-3697,</p>	1,3-5,7	
Y	<p>---</p>	1,3-5,7	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
P, X	<p>TABUCHI M ET AL: "Electrochemical and magnetic properties of lithium manganese oxide spinels prepared by oxidation at low temperature of hydrothermally obtained LiMnO₂" SOLID STATE IONICS, vol. 89, no. 1-2, 1 August 1996, page 53-63 XP004070124 * Page 55: "Results and Discussion" * * table 1 * * Page 54: "Experimental" * ---</p> <p>-/-</p>	8-12	
<p>The present search report has been drawn up for all claims.</p> <p>Place of search Date of completion of the search Examiner MUNICH 22 July 1998 Engl, H</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons & member of the same patent family, corresponding document</p>			



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Category	Citation of document with indication, where appropriate, of relevant passages*	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
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X,D		8-12							
Y	PATENT ABSTRACTS OF JAPAN vol. 095, no. 004, 31 May 1995 & JP 07 010541 A (TOSOH CORP), 13 January 1995, * abstract *	8							
Y	PATENT ABSTRACTS OF JAPAN vol. 095, no. 007, 31 August 1995 & JP 07 101728 A (TOSOH CORP), 18 April 1995, * abstract *	8							
A	US 5 418 090 A (KOKSBANG RENE ET AL) 23 May 1995 * the whole document *	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.6)						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>MUNICH</td> <td>22 July 1998</td> <td>Engl, H</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	MUNICH	22 July 1998	Engl, H
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CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
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